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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 62213A	FOR FURTHER ACTION See Form PCT/PEA/416	
International application No. PCT/US2004/020813	International filing date (day/month/year) 28.06.2004	Priority date (day/month/year) 03.07.2003
International Patent Classification (IPC) or national classification and IPC C07C29/16, C07C45/50, C07C33/03, C07C47/21		
Applicant UNION CARBIDE CHEMICALS & PLASTICS TECHNOLOGY		
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 6 sheets, as follows:</p> <p><input type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (Indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>		
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input checked="" type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input checked="" type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>		
Date of submission of the demand 22.03.2005	Date of completion of this report 10.10.2005	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Cooper, S Telephone No. +49 89 2399-8323	



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Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

Description, Pages

1-39 as originally filed

Claims, Numbers

1, 4-9, 11-16, 19-34 received on 22.03.2005 with letter of 16.03.2005

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

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Box No. IV Lack of unity of invention

1. ☐ In response to the invitation to restrict or pay additional fees, the applicant has:
- ☐ restricted the claims.
 - ☐ paid additional fees.
 - ☐ paid additional fees under protest.
 - ☐ neither restricted nor paid additional fees.
2. ☒ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is
- ☐ complied with.
 - ☐ not complied with for the following reasons:
4. Consequently, this report has been established in respect of the following parts of the international application:
- ☒ all parts.
 - ☐ the parts relating to claims Nos. .

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	7,22-34
	No: Claims	1,4-6,8,9,11-16,19-21
Inventive step (IS)	Yes: Claims	7,22-34
	No: Claims	1,4-6,8,9,11-16,19-21
Industrial applicability (IA)	Yes: Claims	1,4-9,11-16,19-34
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

- D1: US-A-4 269 781 (ZEMA PAUL M ET AL) 26 May 1981 (1981-05-26)
D2: US-A-6 034 286 (EISENSCHMID THOMAS CARL ET AL) 7 March 2000 (2000-03-07)
D3: US 2002/007096 A1 (BRYANT DAVID ROBERT ET AL) 17 January 2002 (2002-01-17)

Section IV.

- 1). Claims 1,4-9,11-16 and 19-21 relate to a method of minimizing degradation of the phosphine ligands used in catalysts for inter alia oxo reactions to α,β -unsaturated aldehydes by selecting appropriate ligands for use in the reaction or specific conditions for the reaction.
- 2). Claims 22-34 relate to a process for reverting the degradation products of (any) phosphine ligands back to the phosphines themselves with no limitation on the reaction conditions under which they arose.
- 3). There is thus no common inventive technical feature linking the method of claims 1,4-9,11-16 and 19-21 with the process according to claims 22 to 34 and consequently a lack of unity.

Section V.

- 1). Claim 1 relates to "a method of minimizing the production of one or more phosphonium ion ligand degradation products". However, the purpose of a process or an effect achieved by a process does not limit it with respect to another process which has all the same process features. Claims 1,6,8,9,11,12,15 and 16 therefore lack novelty with respect to example 11 of D3 (the ligand used has a pKa of 1.36).
- 2). The international examining authority is not in a position to determine whether the features of claims 13 and 14 are given by example 11 of D3. The applicant is seen as bearing the burden of proof in this case.
- 3). In the mixture of example 11 of D3 both 2-pentenal and 3-pentenal are present. Reaction conditions correspond to those mentioned in claims 19-21. Unless the applicant can confirm that no isomerisation of the 3-pentenal to the 2-pentenal is occurring in example 11 of D3, claims 19-21 will also be seen as lacking novelty over this document.

- 4). Example 3 of D2 discloses reaction conditions which fall within the scope of claims 1,4-6,8,9,15 and 16. From column 3, lines 33-57 and claim 13 of the document, it is to be expected that the process of example 3 will produce both 2- and 3-pentenals; as much has been accepted by the applicant in the paragraph bridging pp.4 and 5 of the response dated 22.03.2005. Claims 1,4-6,8,9,11,12,15 and 16 therefore lack novelty over D2, and since isomerisation of 3-pentenal to 2-pentenal under the reaction conditions can be expected to occur, claims 19-21 also lack novelty over D2. It is reiterated that a process claim can not be seen as novel by virtue of any inherency argument. If a prior art process has all the features of a claimed process, the effect of the process will also be given and can not be the basis for novelty. This situation pertains with respect to D2.
- 5). Insofar as it can be assumed that no conjugated aldehyde is formed in the process according to D1, claim 7 can be seen as being novel in that no prior art process for converting polyunsaturated olefins to conjugated aldehydes could be found in the prior art, where the catalyst for the conversion has a ligand selected from the list given in that claim.
- 6). Claims 21-34 are novel because none of D1 to D3 disclose a step where the phosphonium ion degradation products of triorganophosphine ligands are treated with an inert gas, hydrogen, synthesis gas or a combination thereof in a process **separate** from one involving their formation.
- 7). No claims which lack novelty can be accorded an inventive step.
- 8). The object of the present application relating to claims 1,4-9,11-16 and 19-21 is seen in reducing the amount of phosphine ligand degradation occurring in the catalysed preparation of conjugated aldehydes. The solution is seen in using the ligands listed in claim 7. Since no prior art document teaches a link between the particular ligand used and the extent to which it degrades in such reactions, claim 7 is seen as being based on an inventive step.
- 9). The object of the present application relating to claims 22-34 is seen in finding a way to revert the phosphonium ion degradation products of phosphine ligands back to the phosphines. The solution is to treat the degradation products with an inert gas, hydrogen, synthesis gas or a mixture thereof in a step separate from the formation of the degradation products. The degradation products are the result of the reaction of the required conjugated aldehyde product with the phosphine. Since no teaching could be found in the prior art that such degradation products could be reverted to the

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phosphines by the mentioned treatment, there was no incentive to treat the degradation products as claimed in a step separate from the one in which the degradation products are formed and claims 22-34 are based on an inventive step.

Section VII.

The claims are to be numbered consecutively.

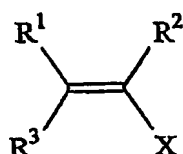
COPY: CLAIMS AS AMENDED UNDER PCT ARTICLE 19

1. A method of minimizing the production of one or more phosphonium ion ligand degradation products in a reaction process wherein a polyunsaturated olefin is reacted in the presence of a transition metal-triorganophosphine ligand complex catalyst to form as a product, by-product, or intermediate product a conjugated functionalized olefin comprising an α,β -unsaturated aldehyde, the minimization method comprising conducting the reaction process with a triorganophosphine ligand having a ligand cone angle greater than 135° or a pKa of less than about 8.3, under process conditions sufficient to minimize the formation of phosphonium ion ligand degradation product(s).
2. Canceled.
3. Canceled.
4. The method of Claim 1 wherein the polyunsaturated olefin conversion is greater than about 80 weight percent and less than about 95 weight percent.
5. The method of Claim 1 wherein the reaction temperature is greater than about 45°C and less than about 95°C .
6. The method of Claim 1 wherein the total pressure is greater than about 300 psig and less than about 5,000 psig.
7. The method of Claim 1 wherein the triorganophosphine ligand is selected from tri-isopropylphosphine, tri-isobutylphosphine, tri-t-butylphosphine, tricyclohexylphosphine, cyclohexyldi-n-butylphosphine, tri(o-methylphenyl)phosphine, dimethylphenylphosphine, methyldiphenylphosphine, and triphenylphosphine, the sulfonated salts of the aforementioned ligands, and any combination of mixtures thereof.
8. The method of Claim 1 wherein the polyunsaturated olefin is a C_{4-60} polyene.
9. The method of Claim 8 wherein the C_{4-60} polyene is selected from the group consisting of butadiene, pentadienes, hexadienes, heptadienes,

octadienes, dicyclopentadiene, hexatrienes, octatrienes, cyclooctadiene, 2,4-pentadienoic acid, 2,4-hexadienoic acid (sorbic), 2,4-decadienoic acid, 2,4-dodecadienoic acid, *cis*-9,*cis*-12-octadecadienoic acid (linoleic), *trans*-9,*trans*-12-octadecadienoic acid (linolelaidic), 5,6-octadecadienoic acid (laballenic), 5,13-docosadienoic acid, 6,10,14-hexadecatrienoic acid (hiragonic), *cis*-9,*cis*-12,*cis*-15-octadecatrienoic acid (linolenic), *cis*-9,*trans*-11,*trans*-13-octadecatrienoic acid (α -eleostearic), *trans*-9,*trans*-11,*trans*-13-octadecatrienoic acid (β -eleostearic), and the mono, di, and tri-glycerol esters and C₁₋₈ alkyl esters of the aforementioned carboxylic acids.

10 10. Canceled.

11. The method of Claim 1 wherein the conjugated functionalized olefin is represented by the formula:



15 wherein X is formyl; and wherein each R¹, R², and R³ is independently selected from hydrogen and C₁₋₆₀ monovalent hydrocarbon radicals, with the proviso that at least one of R¹, R², or R³ is a monovalent hydrocarbon radical.

12. The method of Claim 1 wherein the reaction process comprises hydroformylation.

20 13. The method of Claim 1 wherein the rate of ligand usage is less than about 2 grams ligand per liter reaction fluid per day.

14. The method of Claim 1 wherein the rate of ligand usage is less than about 0.1 gram ligand per liter reaction fluid per day.

25 15. The method of Claim 1 wherein the reaction process comprises contacting a C₄₋₆₀ polyunsaturated olefin with carbon monoxide in the presence hydrogen to form as a product, by-product, or intermediate product an α,β -unsaturated aldehyde.

16. The method of Claim 15 wherein the process is conducted at a polyunsaturated olefin conversion greater than about 80 weight percent and less than about 95 weight percent, or at a temperature greater than about 45°C and less than about 95°C, or at a pressure greater than about 300 psig and less than about 5,000 psig, or at a combination of such process conditions.

17. Canceled.

18. Canceled.

19. A process of minimizing the formation of one or more phosphonium ion ligand degradation products in a reaction process wherein an unconjugated functionalized olefin, characterized as having at least one carbon-carbon double bond in unconjugated position relative to an α -formyl group, is reacted in the presence of a transition metal-triorganophosphine ligand complex catalyst to form as a product, by-product, or intermediate product a conjugated functionalized olefin comprising an α,β -unsaturated aldehyde, the minimization method comprising conducting the reaction process with a triorganophosphine ligand having a cone angle greater than 135° or a pKa less than about 8.3 under process conditions sufficient to minimize the formation of phosphonium ion ligand degradation product(s).

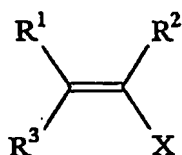
20. The process of Claim 19 wherein the process is conducted to a conversion of unconjugated functionalized olefin of greater than about 80 weight percent and less than about 95 weight percent, or at a temperature greater than about 45°C and less than about 95°C, or at a pressure greater than about 300 psig and less than about 5,000 psig, or at a combination of said process conditions.

21. The process of Claim 19 wherein the unconjugated functionalized olefin is 3-pentenal or an unconjugated unsaturated fatty aldehyde.

22. A process of reverting a phosphonium ion ligand degradation product or mixture of such products back to triorganophosphine ligand(s), the phosphonium ion ligand degradation product or mixture of such products being capable of reversion to useful triorganophosphine ligand and comprising an adduct of a triorganophosphine ligand and a conjugated functionalized olefin comprising an α,β -unsaturated aldehyde; the reversion process being conducted in a reversion

step separate from the process of forming the phosphonium ion ligand degradation product and comprising, treating a reaction product fluid containing the phosphonium ion ligand degradation product or mixture of such products with an inert gas, hydrogen, synthesis gas, or a combination thereof, under conditions sufficient to revert the phosphonium ion ligand degradation product or mixture of such products back to triorganophosphine ligand or mixture of triorganophosphine ligands.

23. The process of Claim 22 wherein the conjugated functionalized olefin is represented by the formula:



wherein X is formyl; and wherein each R¹, R², and R³ is independently selected from hydrogen and C₁₋₆₀ monovalent hydrocarbon radicals, with the proviso that at least one of R¹, R², or R³ is a monovalent hydrocarbon radical.

24. The process of Claim 22 wherein the conjugated functionalized olefin is a C₅₋₆₀ α,β-unsaturated aldehyde.

25. The process of Claim 22 wherein the conjugated functionalized olefin is 2-pentenal or a conjugated unsaturated fatty aldehyde.

26. The process of Claim 22 wherein the triorganophosphine ligand is selected from the group consisting of tri-isopropylphosphine, tri-isobutylphosphine, tri-t-butylphosphine, tricyclohexylphosphine, cyclohexyldi-n-butylphosphine, tri(o-methylphenyl)phosphine, dimethylphenylphosphine, methyldiphenylphosphine, dicyclohexylphenylphosphine, triphenylphosphine, the sulfonated salts of the aforementioned phosphines, and any combination thereof.

27. The process of Claim 22 wherein the inert gas is selected from nitrogen, helium, argon, methane, carbon monoxide, steam, and mixtures thereof.

28. The process of Claim 22 wherein the synthesis gas CO/H₂ comprises a molar ratio from 10/1 to 1/10.

29. The process of Claim 22 wherein the reversion process is conducted at a temperature greater than about 50°C and less than about 150°C.

5 30. The process of Claim 22 wherein the phosphonium ion ligand degradation product comprises an adduct of a triorganophosphine ligand and 2-pentenal; and the reaction product fluid is treated with an inert gas selected from nitrogen, helium, argon, carbon monoxide, methane, and steam, under conditions sufficient to volatilize 2-pentenal and cause reversion of the ligand degradation
10 product back to triorganophosphine ligand.

31. The process of Claim 22 wherein the ligand degradation product comprises an adduct of a triorganophosphine ligand and 2-pentenal; and the reaction product fluid is treated with a source of hydrogen under conditions sufficient to hydrogenate 2-pentenal to pentanal and/or pentanol, thereby reverting
15 the phosphonium ion ligand degradation product back to triorganophosphine ligand.

32. The process of Claim 22 wherein the ligand degradation product comprises an adduct of a triorganophosphine ligand and 2-pentenal; and the reaction product fluid is treated with a source of synthesis gas under conditions
20 sufficient to hydroformylate 2-pentenal, thereby reverting the phosphonium ion ligand degradation product back to triorganophosphine ligand.

33. An integrated process for carbonylation of a polyunsaturated olefin or mixture thereof comprising (a) contacting a polyunsaturated olefin or mixture thereof with carbon monoxide in the presence of hydrogen, and in the presence of a transition
25 metal-triorganophosphine ligand complex catalyst and free triorganophosphine ligand, under process conditions sufficient to prepare a reaction product fluid comprising a transition metal-triorganophosphine ligand complex catalyst, optionally free triorganophosphine ligand, one or more reaction products, by-products, and/or intermediate products including an α,β -unsaturated aldehyde and one or more
30 phosphonium ion ligand degradation products capable of reversion to useful ligand; (b) treating the reaction product fluid from step (a) with an inert gas, hydrogen, synthesis

gas, or a mixture thereof under conditions sufficient to revert the one or more phosphonium ion ligand degradation products back to triorganophosphine ligand; (c) feeding the reaction product fluid taken from step (b), now containing reduced amounts of phosphonium ion ligand degradation products, to a vaporizer or an extractor for separation into a first phase containing reaction products, by-products, and/or intermediate products and a second phase containing transition metal-triorganophosphine ligand complex catalyst and optionally free triorganophosphine ligand; and (d) recycling the second phase from step (c) containing the transition metal-triorganophosphine ligand complex catalyst and optionally free triorganophosphine ligand back to reaction process step (a).

34. An integrated process for carbonylation of a polyunsaturated olefin or a mixture thereof comprising (a) contacting a polyunsaturated olefin or mixture thereof with carbon monoxide in the presence of hydrogen, and in the presence of a transition metal-triorganophosphine ligand complex catalyst and free triorganophosphine ligand, under process conditions sufficient to prepare a reaction product fluid comprising a transition metal-triorganophosphine ligand complex catalyst, optionally free triorganophosphine ligand, one or more reaction products, by-products, and/or intermediate products including an α,β -unsaturated aldehyde, and one or more phosphonium ion ligand degradation products capable of reversion; (b) feeding the reaction product fluid from step (a) to a vaporizer or an extractor for separation into a first phase containing reaction products, by-products, and/or intermediate products, and a second phase containing the transition metal-triorganophosphine ligand complex catalyst, optionally free triorganophosphine ligand, and one or more phosphonium ion ligand degradation products; (c) treating the second phase from step (b) containing the transition metal-triorganophosphine ligand complex catalyst, optionally free triorganophosphine ligand, and phosphonium ion ligand degradation products with an inert gas, hydrogen, synthesis gas, or a mixture thereof under conditions sufficient to revert the phosphonium ion ligand degradation products back to triorganophosphine ligand; and (d) recycling the phase containing the transition metal-triorganophosphine ligand complex catalyst and optionally free triorganophosphine ligand, now containing reduced amounts of phosphonium ion ligand degradation products, back to reaction process step (a).

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